

Excitation mechanisms of sodium night airglow

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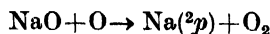
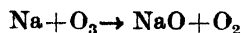
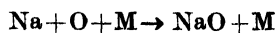
Several known mechanisms contributing to the emission of sodium—*D* lines in the night airglow of the upper atmosphere are examined in detail, using the recently available information about the night-time oxygen-hydrogen atmosphere. Our results establish the following conclusions on firm footing :

- (i) The Chapman mechanism is almost entirely responsible for the observed peak emission at about 85-90 km. altitude.
- (ii) The intensity variation of sodium faithfully follow those of Ozone concentration.
- (iii) The integrated total emission intensity is about 130R.

These calculations are compared with several earlier models and many finer points of the phenomena are brought out.

1. INTRODUCTION

Bernard (1938) as well as Cabannes *et al* (1938) independently reported the discovery of sodium emission in the upper atmosphere. Chapman (1939) initiated the discussion of the photochemistry of sodium which is mainly based upon the following three reactions :



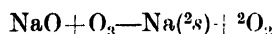
The first two reactions represent the loss (oxidation of free sodium) and the third the production of free sodium atoms (reduction of sodium oxide). This third reaction is usually referred to as the Chapman mechanism, a convention which is also followed here.

Since then the problem is being discussed continuously and vigorously and several excitation mechanisms were suggested and criticised. Table 1 which is adopted from Potter and Del Duka summarizes the state of available information till 1960. Most of these authors have considered that the Chapman mechanism is the principal if not the exclusive source for the excited sodium in the upper atmosphere.

Table 1. Excitation mechanisms for sodium airglow

No.	Excitation mechanism	Proposed by	Criticised by
1	Meteoric Excitation	Cabannes, Dutay & Gauzit (1938)	Chapman (1939)
2	Electron Impact	Russel (1939)	Chapman (1939)
3	Reaction of molecular sodium (Na_2)	Pendor (1950)	Kahn (1950) Ogawa (1954)
4	Neutralization of Na^+	Saha (1951), Mitra (1952)	Saha (1951), Mitra (1952)
5	Scattered light from sunlit side of the earth	Federaro and Donahue (1953)	Hunten (1955)
6	$\text{NaO} + \text{O} \rightarrow \text{Na}(^2\text{P})\text{O}_2$	Chapman (1939) Bates & Nicolet (1950)	Ogawa (1954) Bates (1957)
7	High energy incoming sodium	Bates and Nicolet (1950)	Bates and Nicolet (1950)
8	$\text{NaH} + \text{O} \rightarrow \text{Na}(^2\text{P}) + \text{OH}$	Bates and Nicolet (1950)	Hunten (1967)
9	$\text{NaH} + \text{H} \rightarrow \text{Na}(^2\text{P}) + \text{H}_2$	Bates (1954)	Hingane and Tillu (1976)
10	$\text{NaO} + \text{O}_3 \rightarrow \text{Na}(^2\text{P}) + 2\text{O}_2$	Saxena (1969)	Hingane and Tillu (1976)

Saxena (1969) has recently revived the interest by pointing out that the Chapman mechanism alone can not explain the observed height of the peak of emission layer. He included the reaction



to contribute in the loss of NaO. His calculations indicated a close agreement for the height of the peak of sodium emission layer between observations and theoretical predictions, only after this reaction is included in the total mechanism.

Most of the earlier workers including Saxena, for one reason or another, have not use the appropriate basic data pertaining to night-time oxygen-hydrogen atmosphere. The most crucial parameters for such study are obviously the profiles of NaO_x and O. Battinger (1975), Shimazaki and Laird (1970), and Hunt (1973) Sullivan & Hunten (1964) have give a very critical analysis of such an atmosphere and their models seem to be appropriate for the discussion of the photochemistry of the sodium. The importance of using night time data would be apparent from the figure 1 where the night time atmosphere is compared with the daytime one.

We therefore now propose to re-examine this problem in the context of this recently available information about the night-time oxygen-hydrogen atmosphere.

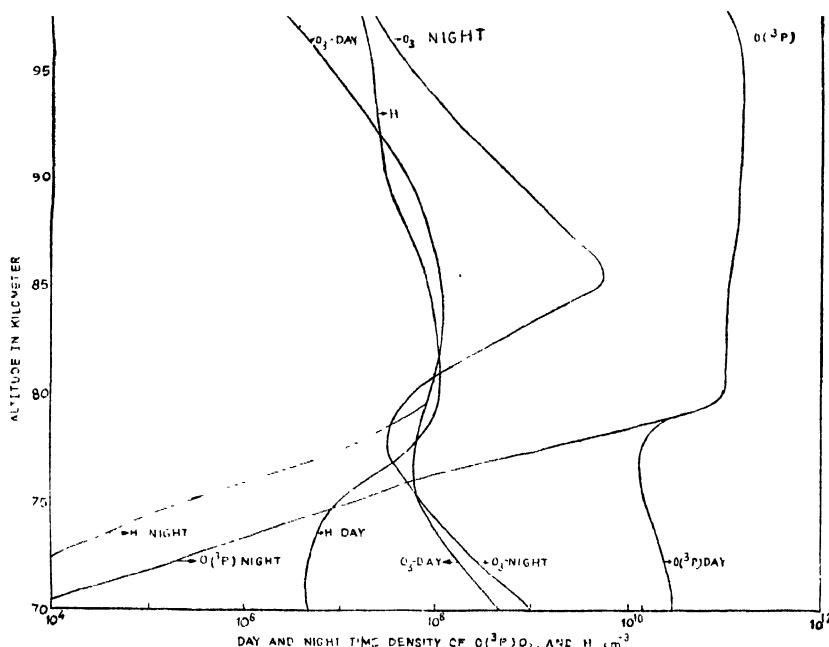


Fig- 1

2. THE PHOTOCHEMICAL MODEL FOR SODIUM

Several proposed photochemical reactions responsible for either production or loss of sodium are collected in Table 2 along with the so far best known or adopted values of rate coefficients of these reactions. It thus appears that, although, information about the concentrations of various species is reviving continuously, (CIRA 1965, 1970) essentially unchanged, since last decades or so.

According to our model, rate of production of $[\text{Na}^2\text{P}]$ is

$$\frac{d}{dt} [\text{Na}^2\text{P}] = k_1[\text{NaO}][\text{O}] + k_7[\text{NaH}][\text{O}] + k_8[\text{NaH}][\text{H}] \quad (1)$$

where $[\text{O}]$ represents the concentration of O etc.

Thus the production of Na^2P depends on this model, on the concentrations of species like NaO , NaH , O and H only. Since concentrations of O and H are assumed from night-time data one need to compute these only or NaO and NaH from the model. These can be immediately written down as below

$$\begin{aligned} \frac{d}{dt} [\text{NaO}] = & k_4[\text{Na}][\text{O}][\text{M}] + k_6[\text{NaO}_2][\text{O}] - k_1[\text{NaO}][\text{O}] - k_3[\text{NaO}][\text{O}][\text{M}] \\ & - k_2[\text{NaO}][\text{O}_3] + k_5[\text{Na}][\text{O}_3] \end{aligned} \quad (2)$$

$$\begin{aligned} \frac{d}{dt} [\text{NaH}] = & k_{10}[\text{NaO}_2][\text{H}] + k_{11}[\text{Na}][\text{H}][\text{M}] - k_8[\text{NaH}][\text{H}] \\ & - k_7[\text{NaH}][\text{O}] - k_9[\text{NaH}][\text{OH}] \end{aligned} \quad (3)$$

Table 2. Photochemical model for sodium emission

No.	Photochemical reaction	Rate coefficient	Reference
R ₁	$\text{NaO} + \text{O} \rightarrow \text{Na}(^2\text{P}) + \text{O}_2$	$k_1 = 2.0 \times 10^{-12}$	Saxena (1969)
R ₂	$\text{NaO} + \text{O}_3 \rightarrow \text{Na}(^2\text{S}) + 2\text{O}_2$	$k_2 = 2.0 \times 10^{-12}$	Saxena (1969)
R ₃	$\text{NaO} + \text{O} \xrightarrow{\text{M}} \text{NaO}_2 + \text{M}$	k_3	Potter and Duna (1960)
R ₄	$\text{Na} + \text{O} \xrightarrow{\text{M}} \text{NaO} + \text{M}$	$k_4 = 7.0 \times 10^{-11}$	Hunten (1967)
R ₅	$\text{Na} + \text{O}_3 \rightarrow \text{NaO} + \text{O}_2$	$k_5 = 3.0 \times 10^{-11}$	Blamont and Donahue (1964)
R ₆	$\text{NaO}_2 + \text{O} \rightarrow \text{NaO} + \text{O}_2$	$k_6 = 9.3 \times 10^{-12}$	Srivastav and Shukla (1970)
R ₇	$\text{NaH} + \text{O} \rightarrow \text{Na}(^2\text{P}) + \text{OH}$	$k_7 = 1.7 \times 10^{-10}$	Srivastav and Shukla (1970)
R ₈	$\text{NaH} + \text{H} \rightarrow \text{Na}(^2\text{P}) + \text{H}_2$	$k_8 = 1.3 \times 10^{-17}$	Srivastav and Shukla (1970)
R ₉	$\text{NaH} + \text{OH} \rightarrow \text{Na}(^2\text{P}) + \text{H}_2\text{O}$	$k_9 = 2.1 \times 10^{-16}$	Srivastav and Shukla (1970)
R ₁₀	$\text{NaO}_2 + \text{H} \rightarrow \text{NaH} + \text{O}_2$	$k_{10} = 3.0 \times 10^{-12}$	Srivastav and Shukla (1970)
R ₁₁	$\text{Na} + \text{H} \xrightarrow{\text{M}} \text{NaH} + \text{M}$	$k_{11} = 4.0 \times 10^{-22}$	Srivastav and Shukla (1970)
R ₁₂	$\text{Na} + \text{O}_2 + \text{M} \rightarrow \text{NaO}_2 + \text{M}$	$k_{12} = 2.0 \times 10^{-33}$	Hunten (1967)

Notes : (i) All rate constants are quoted in centimeter-molecule-second system. For two body and three body reactions units respectively are molecules/cm³ sec and molecules/cm³ sec respectively.

(ii) The rate constants R₆-R₁₁ are taken analogous to ozone-hydrogen reactions Kaufman (1964). Blamont and Donahue (1964) have also used the same concept.

Thus the information about [NaO] and [NaH] can be derived if one knows besides [O], [H] and [O₃] that about [NaO₂]. For this purpose one may write from the model,

$$\frac{d[\text{NaO}_2]}{dt} = k_4[\text{Na}][\text{O}_2][\text{M}] + k_{12}[\text{NaO}][\text{O}][\text{M}] - k_6[\text{NaO}_2][\text{O}] - k_{10}[\text{NaO}_2][\text{H}] \quad \dots (4)$$

As a first approximation, we propose to investigate the steady state of the problem. This approach will only preclude us from studying any nocturnal density variation or any such time dependent phenomena. We therefore assume that the concentrations of NaO, NaH and NaO₂ are constant. Thus eqs. (2), (3) and (4) would reduce to,

$$[\text{NaO}] = \frac{k_4[\text{Na}][\text{O}][\text{M}] + k_6[\text{NaO}_2][\text{O}] + k_5[\text{Na}][\text{O}_2]}{k_1[\text{O}] + k_2[\text{O}_3] + k_3[\text{O}][\text{M}]} \quad \dots (5)$$

$$[\text{NaH}] = \frac{k_{10}[\text{NaO}_2][\text{H}] + [\text{Na}][\text{H}][\text{M}]}{k_7[\text{H}] + k_8[\text{O}] + k_9[\text{OH}]}$$

$$[\text{NaO}_2] = \frac{k_4[\text{Na}][\text{O}_2][\text{M}] + k_{12}[\text{NaO}][\text{O}][\text{M}]}{k_6[\text{O}] + k_{10}[\text{H}]} \quad \dots (7)$$

Eqs (5) and (7) are interlinked, but the values of those concentrations viz (NaO) and $[\text{NaO}_2]$ are found to be stabilized after few iterations.

3. RESULTS AND DISCUSSION

(i) Production of $\text{Na}(^2P)$:

We compare in figure 2 results of our computations with those of Saxena to illustrate the differences that arise due to use of proper night-time data. It is thus evident that we do not experience the difficulty noted by Saxena about the height of peak of emission layer for sodium. The peak itself appears at 85 km and thus closely agrees with the experimental observations as shown in figure 3. For the sake of comparison, peaks both in observations and calculations are scaled to unity.

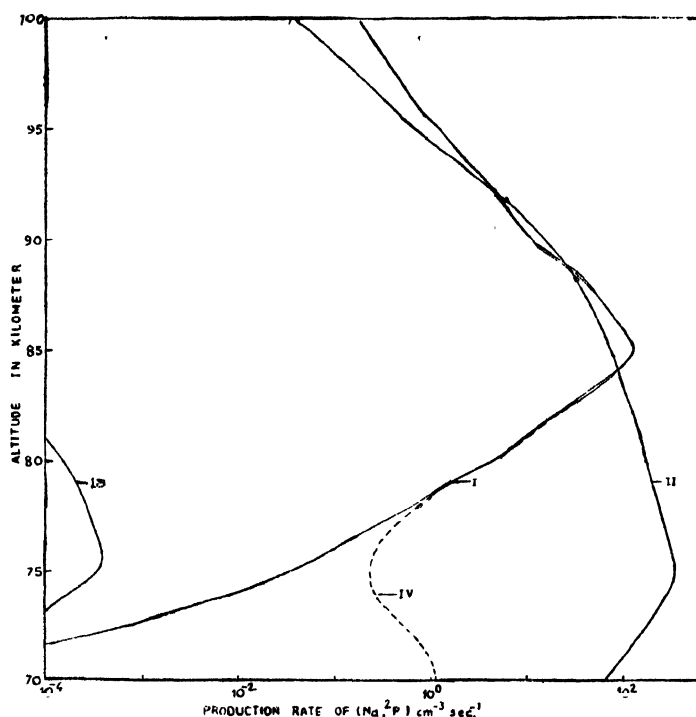


Fig. 2

We may further mention that reaction R_7 , R_8 , and R_9 suggested respectively by Bates and Nicolet (1950), Bates (1954) and Shivastav *et al* (1970) contribute negligibly in the present model. These results are therefore consistent with earlier models.

Thus the present model re-establishes that the Chapman mechanism is almost entirely responsible for the production of sodium emission.

We now wish to examine the model more closely by analyzing the behaviour of other important species viz NaO, NaO₂ and NaH of this model.

(ii) *The density of NaO*

It is evident from eq. (1) and the results presented in figure 2, that the most important species for the production of Na(²P) is NaO itself. The photochemical model for [NaO] is given by eq.(2) in which we note that in the denominator

$$k_1[\text{O}] + k_2[\text{O}_3] \gg k_3[\text{O}][\text{M}]$$

at all heights. Hence we neglect this term for all subsequent computations and present in figure 4 the contributions of R_1 , R_5 and R_6 separately, alongwith the

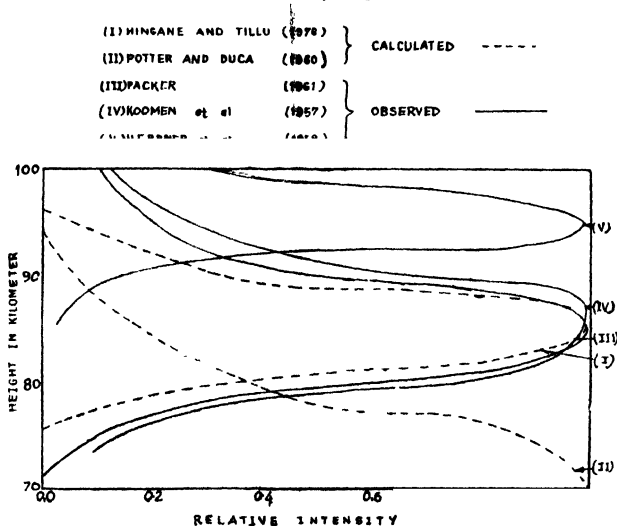


Fig. 3

total density of sodium monoxide. We find that although R_5 dominates at all heights, the contribution of R_6 is also comparable between the heights 70 to 75 km. Both of these reactions have been included in Chapman mechanism itself by Srivastav and Shukla (1970).

We now comment upon the importance of Saxena's suggestion in the over all context of the model when applied to new night-time data. The importance of the Saxena's suggestion is determined by the relative magnitudes of terms $k_1[\text{O}]$ and $k_2[\text{O}_3]$ in the denominator at different heights. For the heights above 75 km the oxygen term predominates and Saxena's suggestion loses its significance as reflected in figure 2. However it does retain some ground in the range of heights between 70-75 km. To illustrate this point we present our computations by dropping the terms $k_2[\text{O}_3]$ in the denominator of eq. (2). The results are presented as dotted lines in figure 2 and figure 4. The density of NaO now shoots up to 10^8

cm^{-3} at 70 km and produces a secondary maxima in figure 2. for the production of $\text{Na}(^2\text{P})$. Thus Saxena's suggestion is still quite important in this height region for the density of NaO and to a certain extent for the production of $\text{Na}(^2\text{P})$.

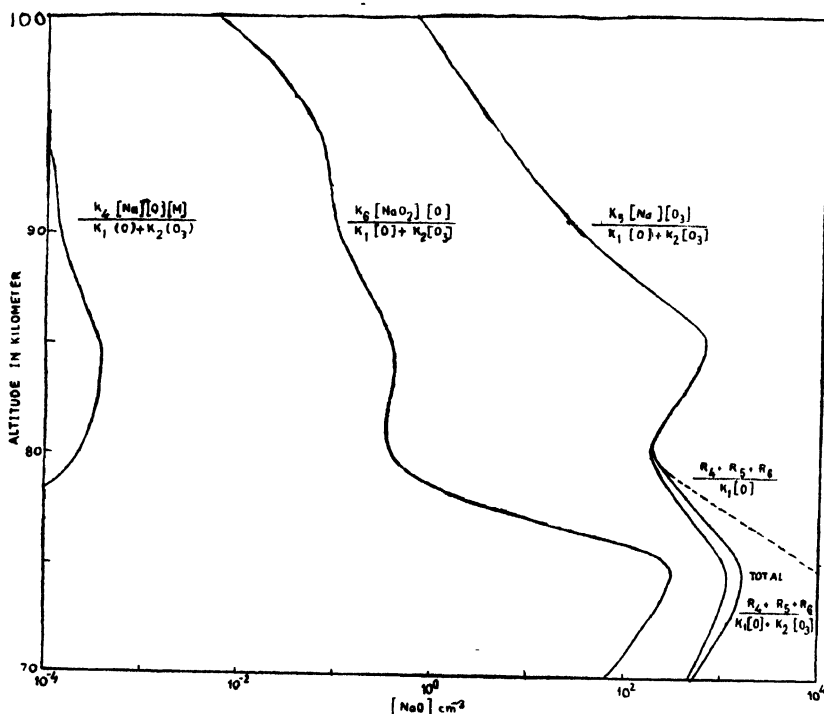


Fig. 4

(iii) *The density of NaO_2 and NaH*

We find a very negligible role played by NaH in the over all model. However that of NaO_2 is not that negligible and at least assumes importance around the heights 70-75 km. Out of the two reactions contributing to the production of NaO_2 , R_{12} is predominant and hence one noted that the three body recombination reaction does play some role in the entire model at least for the heights around 70-75 km.

(iv) *Intensity of Sodium Night Airglow*

Intensity of the sodium night airglow can be obtained from the results obtained for the production rate Q of $\text{Na}(^2\text{P})$ (figure 2) and using the formula

$$I = 10^{-6} \int_{h_1}^{h_2} Q dh \quad \text{Rayleigh} \quad \dots (8)$$

where h_1 and h_2 correspond to the lower and the upper height limits viz. 70 to 110 km. This gives a value of $I \sim 130R$ approximately for the total intensity which can be compared with the mean intensity $\sim 100R$ reported at this station by Chiplonkar and Tillu (1967) or at any station either in temperate or tropical latitude.

(v) *Sodium Night Airglow and the Ozone density*

Since the Chapman mechanism contribute almost exclusively to the production of $\text{Na}(^2\text{P})$ eq. (1) can be approximated as

$$\frac{d[\text{Na}, ^2\text{P}]}{dt} \simeq k_1[\text{NaO}][\text{O}] \quad \dots (9)$$

At 85 km and around where $[\text{Na}^2\text{P}]$ shows a peak, eq. (5) can also be approximated as

$$[\text{NaO}] \simeq \frac{k_5[\text{Na}][\text{O}_3]}{k_1[\text{O}]} \quad \dots (10)$$

which when substituted back in eq. (9) yields

$$\frac{d[\text{Na}, ^2\text{P}]}{dt} \simeq k_5[\text{Na}][\text{O}_3] \quad \dots (11)$$

It is thus apparent that variations in O_3 should be reflected faithfully in the observed variations of sodium night airglow intensity. This conclusion is thus consistent with the comments of earlier investigators (Omhalp 1957, Ballif and Venkateshwar 1963).

4. CONCLUDING REMARKS

We may mention the following two points for further improvement in the model use by us.

- (i) We have substituted the left hand sides of eqs. (2), (3) and (4) each equal to zero as a first approximation. This is not really necessary if one employs a dynamic model. We are progressing in this direction.
- (ii) The second defect of the present model is the lack of adequate laboratory data on reaction rate coefficients.

This knowledge will further improve the numerical computations when coupled with the results of the dynamic model.

Origin of the sodium in the upper atmosphere has recently been considered in quite detail by Fiocco and Visconti (1973), Visconti (1973) Ved. Mitra (1974), Ghosh and Mitra (1974) and Baggalay (1975). We feel that these allied studies will have a definite bearing and will contribute in future in further understanding of the excitation mechanisms of sodium night airglow.

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REFERENCES

- Baggalay W. 1975 *Nature* **257**, 567.
- Ballif J. R. and Venkateswaran S. V. 1963 *J. Atmos. Sci* **20**, 255.
- Bates D. R. 1954 *The earth as a planet* Ed. G. P. Kuiper, Chicago University Press, Chicago, 576
- Bates D. R. 1957 *The threshold of Space*, Pergamon Press, pp 14-21 (1957).
- Bates D. R. and Nicolet M. 1950 *J. Geophys. Res.* **55**, 235.
- Battaner E. 1975 *J. Atmos. Terr. Phys.* **37**, 1155.
- Bernard R 1938a *Zeits. f. Physik* **119**, 291.
- Bernard R. 1938 1938b *Comptes Rendus Acad. Sci.* (Paris) **206**, 928.
- Blamont J. E. and Donahue T. M. 1964 *J. Geophys. Res.* **69**, 4093.
- Cabannes J., Dufay J. and Gauzit J. 1938 *Comptes Rendus Acad. Sci.* (Paris) **206**, 1525.
- Chapman S. 1939 *Astro. J.* **90**, 309.
- Chiplonkar M. W. and Tillu A. D. 1967 *Indian J. Pure Appl. Phys.* **15**, 87.
- Cira (Cispar Internatilnal Reference Atmosphere) North-Holland Publishing company Amsterdam (1965), (1970).
- Federaro and Donahue T. M. 1953 *Phys. Rev.* **91**, 1561.
- Heppner J. P. and Meredith L. H. 1958 *J. Geophys. Res.* **63**, 51.
- Fioeco and Visconti 1973 *J. Atmos and Terr. Phys.* **35**, 165.
- Fioeco G., Fua D. and Viscounti G. 1975 *Ann. Geophys.* (France) **30**, 517.
- Ghosh S. N. and Mitra V. 1974 *Indian J. Phys.* **48**, 1.
- Hunt B. G. 1973 *J. Atmos. Terr. Phys.* **33**, 1869.
- Hinten D. M. 1955 *Phys. Rev.* **97**, 1178.
- Hunten D. M. 1967 *Space Sci. Rev.* **6**, 493.
- Kahn F. D. 1950 *Phys. Rev.* **79**, 167
- Kaufman F. 1964 *Ann. de Geophys.* **20**, 106.
- Kooman M. J., Scolnik R. and Tousey R. 1959 *Direct measurements of the night airglow The threshold of Space* (Ed. M. Zelikoff). Pergamon Press, London & New York, pp.217.
- Mitra S. K. 1952 *The upper atmosphere* (2nd Ed.) Asiatic Society, Calcutta.
- Mitra V. 1974 *Ann. Geophys.* (France) **30**, 421.
- Ogawa M. 1954 *Sci. Light.* (Tokyo) **3**, 47.
- Omholt A. 1957 *J. Geophys. Res.* **62**, 207.
- Packer D. M. 1960 *J. Geophys. Res.* **65**, 3915.
- Pondlrf R. 1950 *Phys. Rev.* **78**, 66.
- Potter A. E. and Del Duga 1960 *J. Geophys. Res.* **65** 3915.
- Russell H. N. 1939 *Sci. American* **160**, 88.
- Saha A. K. 1951 *Indian J. Phys.* **25**, 375.
- Saxona P. P. 1969 *Ann. Geophys.* **25**, 847.
- Shimazaki T. and Laird A. R. 1970 *J. Geophys. Res.* **75**, 3221.
- Srivastav A. N. and Shukla R. V. 1970 *Ann. Geophys.* **26**, 501.
- Sulltvan H. M. and Hunten D. M. 1964 *Canad. J. Phys.* **42** 937.
- Visconti G. 1973 *J. Atmos. Terr. Phys.* **35**, 1331.